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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

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1.	Your reference	Q036334PGB
2.	Patent application number *(The Patent Office will fill in this part)*	19 JUL 1997 **9715175.7**
3.	Full name, address, and postcode of the or of each applicant *(underline all surnames)*	The University of Birmingham, Edgbaston, Birmingham, B15 2TT, England.
	Patents ADP number *(if you know it)*	7736845001
	If the applicant is a corporate body, give the country/state of its incorporation	England.
4.	Title of the invention	METHOD OF CASE HARDENING
5.	Name of your agent *(if you have one)*	Marks & Clerk
	"Address for Service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Alpha Tower Suffolk Street Queensway Birmingham B1 1TT
	Patents ADP number *(if you know it)*	18002
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country / Priority application number *(if you know it)* / Date of filing *(day / month / year)*
7.	If this application is divided or otherwise derived from an earlier UK application give the number and filing date of the earlier application	Number of earlier application / Date of filing *(day / month / year)*
8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	YES

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form	
Description	7
Claim(s)	
Abstract	
Drawing(s)	2

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature

Date 18 July 1997

12. Name and daytime telephone number of person to contact in the United Kingdom — Anthony R. Pearce 0121 643 5881

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METHOD OF CASE HARDENING

This invention relates to a method of case hardening and is more particularly concerned with a method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium.

According to the present invention, there is provided a method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium, said method comprising the steps of (a) heat-treating the article formed of titanium, zirconium or alloy of titanium and/or zirconium in an oxidising atmosphere at a temperature in the range of 700 to 1000°C so as to form an oxide layer on the article; and (b) further heat-treating the article in a vacuum or in a neutral or inert atmosphere at a temperature in the range of 700 to 1000°C so as to cause oxygen from the oxide layer to diffuse into the article.

The time for heat-treatment in step (a) is relatively short and depends, inter alia, upon the nature of the oxidising medium and the intended use of the article. Typically, the time may be, for example, from 0.1 to 1 hours, preferably 0.4 to 0.6 hours.

Both theoretical and experimental work has shown that significant improvements in the load-bearing capacity of a hard coating/sub structure system can be achieved provided that, in addition to a high interfacial adhesion strength, the substrate can firmly withstand the applied load without appreciable plastic deformation. This means that deep case surface engineering processes are beneficial for hard thin coatings on titanium alloys in view of their inherent low yield strengths and low elastic moduli. However, most titanium alloys, unlike ferrous materials,

cannot be hardened to a great extent by convention surface engineering techniques since there is no hardening reaction in titanium alloys comparable to the martensite transformation in ferrous materials. Notwithstanding the fact that titanium alloys can be deeply hardened by electron beam surface alloying, it is still difficult in practice to achieve controlled reproducibility of composition in the alloyed surface layer. Oxidising titanium alloys at a high oxidation temperature for an extended period of time can also product a deep hardened case. However, simple oxidation at higher temperatures (greater than 700°C) is prone to the formation of severe scaling, resulting in a crumbly surface oxide layer. The present invention avoids this by oxidation treatment at an elevated temperature effected for a relatively short period of time, followed by the subsequent heat treatment operation. During the subsequent heat treatment operation effected substantially in the absence of oxygen, it is believed that the oxide dissolves at the oxide/metal interface and that oxygen is absorbed by the titanium via the overall reaction:-

$TiO2(S) + Ti(S) = 2O$ (dissolved in Ti)

Thus, the surface oxide produced by the previous oxidising step serves as an oxygen reservoir and thus a high oxygen potential will be maintained at the oxide/titanium interface until the oxide has totally disappeared. The oxygen diffuses inwardly into the surface of the article due to the steep oxygen gradient in the diffusion zone to produce the desired deep hardening effect. Once the oxide layer has dissolved, there is no further input of oxygen into the metal lattice, and the inward diffusion gives rise to a slight lowering of the surface hardness to a level of about 750 HV.

The heat-treatment in step (a) is conveniently effected at atmospheric pressure.

Steps (a) and (b) may be repeated at least once.

Conveniently, the oxidising atmosphere in step (a) is air. The temperature in step (a) is preferably 700 to 900°C, more preferably 800 to 900°C, and most preferably about 850°C.

The temperature in step (b) is preferably 700 to 900°C, more preferably about 800 to 900°C, and most preferably about 850°C. In the case where the heat treatment in step (b) is effected in a vacuum, the pressure is preferably not more than 1.3×10^{-2} Pa (1×10^{-4} Torr) Pa, and is conveniently about 1.3×10^{-4} Pa (1×10^{-6} Torr).

Where the heat treatment in step (b) is effected in an inert or neutral atmosphere, any non-oxidising and non-reducing atmosphere may be employed, such as argon or other inert gas containing no or only a low partial pressure of oxygen.

The time required for the heat treatment in step (b) is typically in the range of 10 to 30 hours and may conveniently be about 20 hours.

It is within the scope of the present invention to follow the treatment steps (a) and (b) with any of a variety of subsequent treatments or processes to reduce friction. In particular, it is within the scope of the present invention to follow the method of the present invention with the treatment method disclosed in our copending British Patent Application No. 9614967.9 for improving the tribological behaviour of a titanium or titanium alloy article. Such process basically involves the gaseous oxidation of the article at a temperature in the range of 500 to 725°C for 0.5 to 100 hours, the temperature and time being selected such as to

produce an adherent surface compound layer containing at least 50% by weight of oxides of titanium having a rutile structure and thickness of 0.2 to 2μm on a solid solution - strengthened diffusion zone where the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50μm.

The present invention is applicable to commercially pure grades of titanium, titanium alloys (α,$\alpha+\beta$, or β alloys), commercially pure grades of zirconium, zirconium alloys and to alloys of zirconium and titanium.

Where the article is required to have good fatigue properties, it may be subjected to a mechanical surface treatment, such as shot peening, after heat treatment in order to restore the fatigue properties which may be reduced by the heat treatment operation.

In the accompanying drawings:-

Fig 1 is an SEM micrograph showing the overall microstructure of a sample of an oxygen-diffused (OD) Ti6Al4V material treated in accordance with the method of the present invention,

Fig 2 is a graph showing microhardness profiles for the OD Ti6Al4V material produced in accordance with the present invention and for other surface-treated articles formed of the same material (Ti6Al4V), and

Fig 3 is a graph showing the effect of OD treatment and OD plus shot peening (OD+SP) on the fatigue properties of Ti6Al4V.

Samples of Ti6Al4V in the form of cylindrical coupons of 5 mm thickness, cut from a 25 mm diameter bar were used. The samples were then thoroughly cleaned and subsequently thermally oxidised at 850°C for 30 minutes in air in a muffle furnace. After being allowed to cool,

the samples were subjected to a further heat treatment operation at 850°C for 20 hours in a vacuum furnace (about 1×10^{-4} Pa about 10^{-6} Torr). Alternatively, the steps of (a) thermal oxidation and (b) further heat treatment can be carried out in a single vacuum furnace, step (a) being effected in air and step (b) being effected at 1×10^{-4} Pa after evacuation of the air.

It was noted that, after thermal oxidation at 850°C for 30 minutes, the samples had a dark brown appearance. However, this changed to silver following the further heat treatment operation. The metallography of the oxygen-diffused treated sample is shown in Fig 1. A hardened layer was produced which was which was estimated from the transition in morphology to have a depth of about 300μm and appeared (from the different etching effects) to consist of two sub-layers, the first sub-layer having a depth of about 80μm and the second sub-layer, lying under the first sub-layer, having a depth of about 220μm.

A typical microhardness profile for the above-treated samples is illustrated in Fig 2 where, for comparison purposes, microhardness profiles are also given for samples of the same Ti6Al4V material treated by one of three processes, namely oxidation at 850°C for 30 minutes, oxidation at 850°C for 20.5 hours and plasma nitriding at 850°C for 20 hours in an atmosphere of 25% N_2 and 75% H_2. It is notable that the OD material treated in accordance with the present invention showed a more pronounced hardening effect in terms of higher hardness and deep-hardened zone than the thermally oxidised material with the same thermal cycle (850°C/20.5 hours). The microhardness profile for the OD material in accordance with the present invention is in good agreement with the observed two-layer microstructural features illustrated in Fig 1.

As can be seen from Fig 2, the OD samples produced in accordance with the present invention had a high hardness (greater than 700 $HV_{0.05}$) plateau in the first 80μm and a total hardened layer of about 300μm in depth.

As can be seen from Fig 3, OD treatment in accordance with the present invention reduces the fatigue properties of Ti6Al4V. However, the reduction in the fatigue limit was totally restored and slightly elevated by about 30 MPa over the untreated material by shot peening. In this particular case, the shot peening was effected using C glass shot with an Almen density of 0.15-0.029N.

As noted above, the samples treated in accordance with the present invention possessed a significantly greater depth of hardening effect than a direct oxidation treatment at the same temperature and for the same total time (850°C/20.5 hours). This means that the treatment in accordance with the present invention not only avoids the formation of an undesirable scale, which always occurs as a result of oxidation treatment at high temperature, but also confers a greater case hardening effect. This phenomenon at first seems difficult to understand since, in both instances, a high oxygen potential exists at the air/oxide interface for the oxidation treatment or at the oxide/Ti interface for the treatment in accordance with the present invention. It is known that oxidation of titanium is controlled by oxygen diffusion in the diffusion zone rather than in the oxide, since the diffusion coefficient for oxygen in TiO2 is about 50 times that in α-Ti at the same temperature. Therefore, there is no reason to relate to the difference in the hardening effect between the process of the present invention conducted at 850°C for a total time of 20.5 hours and a simple oxidation treatment effected at 850°C for 20.5

hours, to the diffusion resistance of oxygen passing through the oxide layer.

Without prejudice to the present invention, it is theorised that the above phenomenon is caused by the retarding effect of nitrogen (from the air) on the diffusion of oxygen. During prolonged treatment in air, a build-up of nitrogen atoms may occur at the oxide/metal interface (see A.M. Chaze et al, Journal of Less-Common Metals, 124 (1986) pages 73 to 84) and may act as a block on the inward diffusion of oxygen. In the above described process according to the present invention, no further nitrogen is admitted during vacuum treatment and the blocking effect is therefore much reduced. Thus, it is presently believed to be significant in the method of the present invention to minimise the presence in the heat-treatments of step (b) of elements which are capable of bonding to the surface of the article being treated.

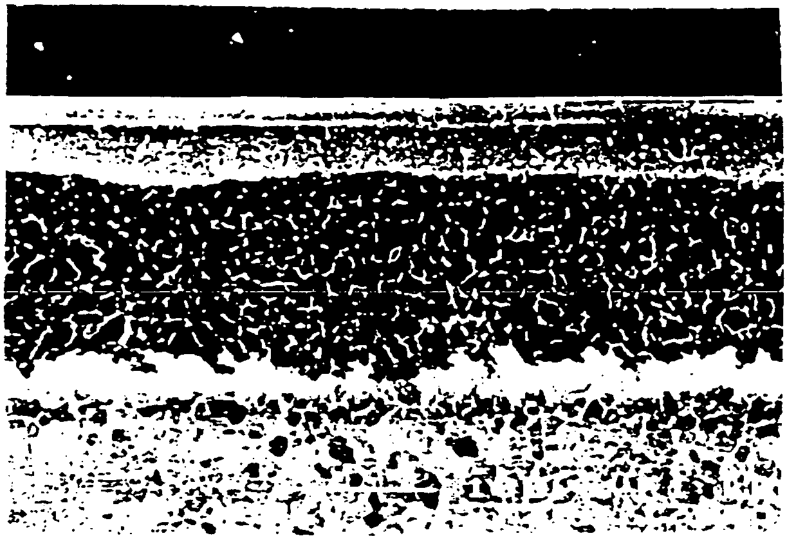


Figure 1 SEM micrograph showing overall microstructure of OD treated material

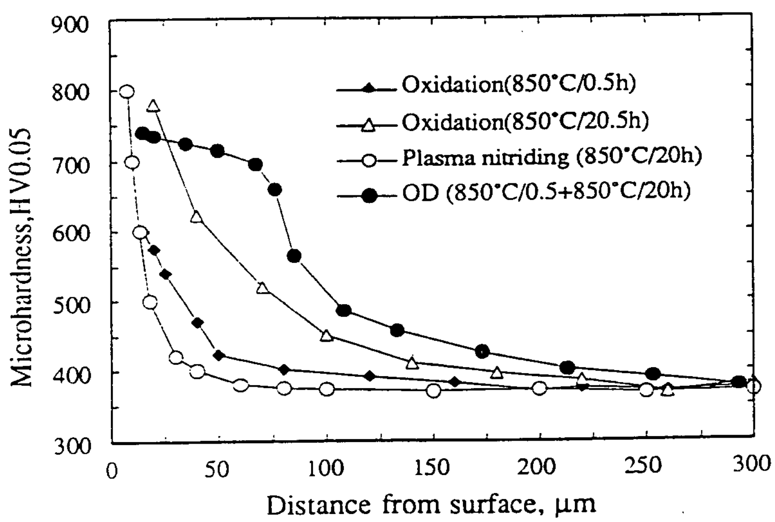
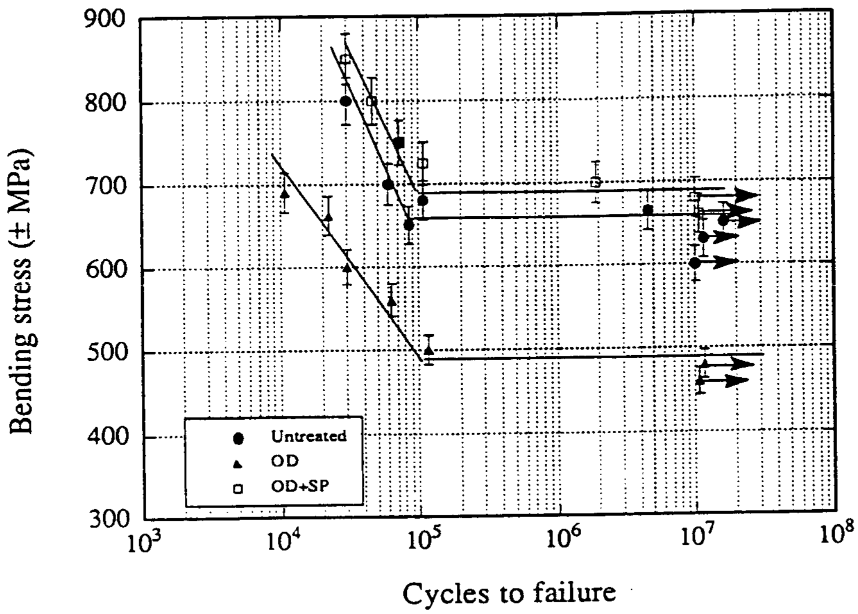


Figure 2 Microhardness profiles for oxygen surface engineered Ti6Al4V.



(b)

Figure 3 Effect of OD treatment (OD) and OD plus shot peening (OD+SP) on fatigue properties of Ti6Al4V.

① 98/02082

② 15 July 98

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